

## Electronic Supporting Information

### Imidazolium-functionalized $\beta$ -cyclodextrin as highly recyclable multifunctional ligand in water

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## Materials and characterization

All organic compounds were obtained commercially and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on 500 and 400 MHz spectrometers in the indicated solvent. Chemical shifts are reported in ppm with internal reference to TMS, and J values are given in Hertz. Synthesis of the mono-tosyl  $\beta$ -CD (**2**) from the tosyl precursor **1** and the ligand precursor **6** are performed as reported in the literature.<sup>1-2</sup> Size distributions in aqueous solutions at 25, 75 and 90°C were obtained on a Malvern Zetasizer Nano ZS instrument operating at a fixed angle of 173°.

### 1-Dodecyl-imidazole **3**

Under  $\text{N}_2$  atmosphere, a solution of NaH (29.3 mmol) in 1,4-dioxane (8mL) was added drop wise to a solution of imidazole (14.7 mmol) in 1,4-dioxane (8mL). The reaction media is then heated at 90 °C during 1 h. A pink color is observed. Afterwards, a solution of 1-bromododecane (14.7 mmol) in 1,4-dioxane (10mL) is added and the reaction media is heated at 90 °C during 48 h. The mixture change color from pink to pale yellow. 1,4-dioxane is then removed *in vacuo* and 125 mL of water was added. Product was extracted with 3 x 25 mL of  $\text{CH}_2\text{Cl}_2$ . After drying over  $\text{MgSO}_4$ , the solvent was evaporated *in vacuo* and the desired product is obtained as a dark orange liquid (10.29 mmol, 70 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.48 (s, 1H), 7.08 (s, 1H), 6.93 (s, 1H), 3.94 (t,  $J$  = 8 Hz, 2H), 1.83-1.74 (m, 2H), 1.35-1.26 (m, 18H), 0.88 (t,  $J$  = 8Hz, 3H)  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 137.02, 129.21, 118.75, 47.1, 31.94, 31.08, 29.59, 29.51, 29.43, 29.33, 29.07, 26.55, 22.68, 14.12 HRMS (ESI): calculated for  $\text{C}_{15}\text{H}_{28}\text{N}_2$  237.2331, found 237.23253.

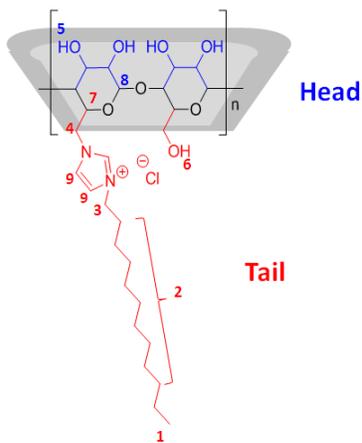
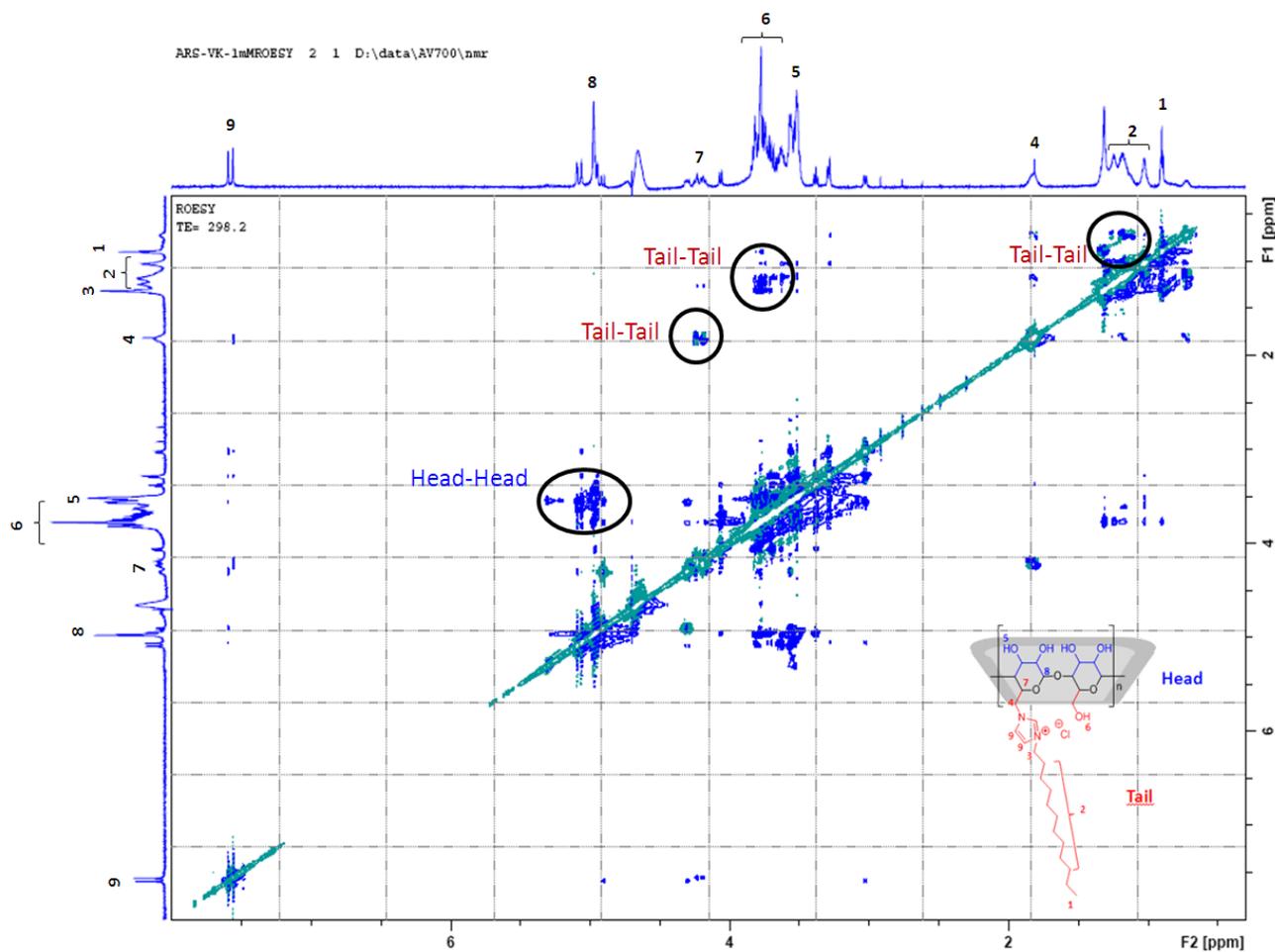
### 1-Dodecyl-2-methyl-imidazole 3.1

Under N<sub>2</sub> atmosphere, a solution of NaH (29.3 mmol) in 1,4-dioxane (8mL) was added drop wise to a solution of 2-methyl-imidazole (14.7 mmol) in 1,4-dioxane (8mL). The reaction media is then heated at 90 °C during 1 h. Afterwards, a solution of 1-bromododecane (14.7 mmol) in 1,4-dioxane (10mL) is added and the reaction media is heated at 90 °C during 48 h. 1,4-dioxane is then removed *in vacuo* and 125 mL of water was added. Product was extracted with 3 x 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. After drying over MgSO<sub>4</sub>, the solvent was evaporated *in vacuo* and the desired product is obtained as a orange liquid (11.76 mmol, 80 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 6.93 (s, 1H), 6.83 (s, 1H), 3.84 (t, *J* = 8 Hz, 2H), 2.41 (s, 3H), 1.79-1.69 (m, 2H), 1.38-1.24 (m, 18H), 0.91 (t, *J* = 8Hz, 3H) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ = 127.08, 119.07, 46.14, 31.96, 30.82, 29.61, 29.55, 29.47, 29.34, 29.19, 26.62, 22.70, 14.14, 13.09 HRMS (ESI): calculated for C<sub>16</sub>H<sub>23</sub>N<sub>2</sub> 251.24818, found 251.24916.

### Dodecyl imidazolium modified β-CD 4

Under N<sub>2</sub> atmosphere, 1-dodecyl-imidazole **3** (0.66 mmol) was added to solution of a dried mono-tosyl-β-CD **2** (0.22 mmol) in 1 mL DMF. The reaction media was heated at 90 °C during 48 h. the reaction mixture was then cooled to room temperature and the product was precipitated with acetone (4 mL). The solid was collected by filtration and washed with acetone (2 x 2 mL). Pure product is obtained via acetone diffusion in DMF. The solid was then dissolved in deionised water (12 mL) and anion exchange from tosylate to chloride was performed using an Amberlite IRA-410 Cl<sup>-</sup> resin to yield **4** as a light yellow solid (0.12 mmol, 55 %). <sup>1</sup>H NMR (DMSO, 500 MHz): δ = 9.11 (s, 1H), 7.80 (s, 1H), 7.73 (s, 1H), 5.95 (d, *J* = 4 Hz, 1H), 5.85-5.63 (m, 13H), 4.97 (s, 1H), 4.89-4.76 (m, 8H), 4.58-4.46 (m, 6H), 4.34-4.29 (m, 1H), 4.18-4.13 (m, 2H), 3.98 (t, *J* = 5Hz, 1H), 3.88-3.81 (m, 2H), 3.75-3.70 (m, 2H), 3.68-3.52 (m, 20H), 3.49-3.41 (m, 4H), 3.33-3.25 (m, 5H), 3.21-3.19 (m, 1H), 3.09-3.05 (m, 1H), 2.86-2.81 (m, 1H), 2.51 (s, 3H), 1.83-1.77 (m, 2H), 1.32-1.18 (m, 17H), 0.86 (t, *J* = 5Hz, 3H) <sup>13</sup>C NMR (D<sub>2</sub>O, 500 MHz): δ = 134.47, 124.74, 122.76, 102.63, 102.58, 102.23, 102.10, 82.94, 82.39, 81.14, 80.95, 80.89, 80.80, 73.19, 73.11, 73.05, 73.00, 72.75, 72.00, 71.96, 71.90, 71.88, 71.84, 71.76, 71.72, 71.60, 71.53, 61.42, 59.74, 59.63, 59.53, 59.21, 50.09, 48.87, 30.50, 28.71, 28.50, 28.02, 27.76, 27.60, 27.32, 25.79, 23.38, 21.42, 13.50 HRMS (ESI): calculated for C<sub>57</sub>H<sub>97</sub>N<sub>2</sub>O<sub>34</sub> 1353.59135, found 1353.59172.

## 2D ROESY <sup>1</sup>H NMR experiment



**Figure S1:** 2D ROESY <sup>1</sup>H NMR experiment recorded on a 1 mM solution of **4** (D<sub>2</sub>O, 700 MHz, 25°C). Protons are numbers and color identified.

## 2-Methyl-dodecyl imidazolium-modified $\beta$ -CD **5**

Under  $N_2$  atmosphere, 1-dodecyl-2-methyl-imidazole **3.1** (0.23 mmol) was added to solution of a dried mono-tosyl- $\beta$ -CD **2** (0.69 mmol) in 1.5 mL DMF. The reaction media was heated at 130 °C during 48 h. The reaction mixture was then cooled to room temperature and the product was precipitated with acetone (4 mL). The solid was collected by filtration and washed with acetone (2 x 2 mL). Pure product is obtained via acetone diffusion in DMF. The solid was then dissolved in deionised water (14 mL) and anion exchange from tosylate to chloride was performed using an Amberlite IRA-410  $Cl^-$  resin to yield **5** as a light yellow solid (0.10 mmol, 43 %).  $^1H$  NMR (DMSO, 400 MHz):  $\delta$  = 7.70 (s, 1H), 7.63 (s, 1H), 5.98 (d,  $J$  = 8 Hz, 1H), 5.90-5.65 (m, 13H), 4.96 (s, 1H), 4.89-4.79 (m, 6H), 4.73-4.68 (m, 2H), 4.57-4.43 (m, 6H), 4.38-4.35 (m, 1H), 4.09-4.03 (m, 2H), 4.00-3.93 (m, 2H), 3.89-3.80 (m, 3H), 3.76-3.50 (m, 20H), 3.46-3.32 (m, 10H), 3.00 (s, 1H), 2.70-2.66 (m, 1H), 2.59 (s, 3H), 2.55 (s, 3H), 1.78-1.70 (m, 2H), 1.32-1.18 (m, 17H), 0.87 (t,  $J$  = 8Hz, 3H)  $^{13}C$  NMR (DMSO, 500 MHz):  $\delta$  = 145.69, 122.33, 121.75, 102.72, 102.57, 102.39, 102.27, 101.86, 84.08, 83.16, 82.11, 81.97, 81.89, 81.80, 73.82, 73.53, 73.42, 73.29, 73.10, 73.03, 72.88, 72.79, 72.72, 72.66, 72.52, 72.02, 70.79, 61.25, 60.53, 60.43, 60.37, 60.24, 59.37, 49.08, 48.16, 36.28, 31.75, 31.25, 31.16, 29.45, 29.15, 28.97, 26.27, 22.53, 14.10, 10.10 HRMS (ESI): calculated for  $C_{58}H_{99}N_2O_{34}$  1367.60737, found 1367.60801.

## General procedure for the surface tension measurements

Water (20 mL) was heated to the desired temperature in a Dataphysics DCAT11 surface tension analyser. Various amounts of a concentrated solution of **4** in water (10 mM) were added and the mixture was stirred for 1 min. The stirring was stopped before the measurement. The surface tension was then recorded using a rectangular Wilhemy plate.

**Table S1:** Surface tension measurement for **4** in water at 25°C

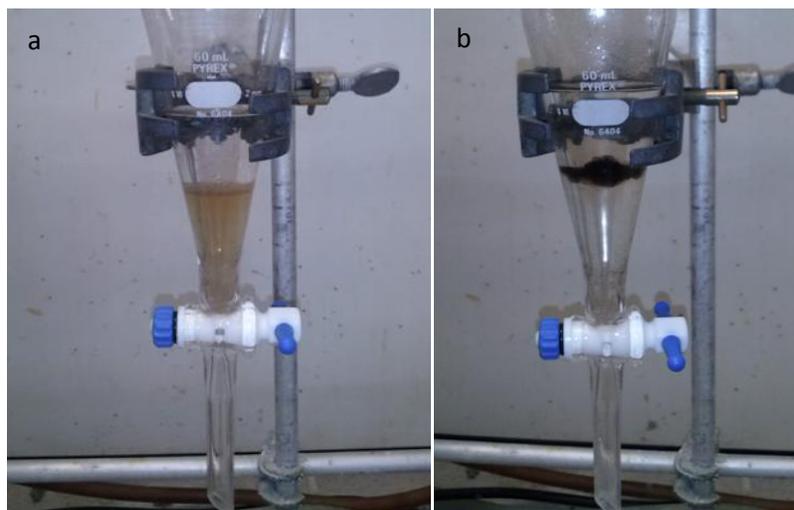
Conc. <sub>cuvette</sub> ( $\mu\text{M}$ )	Pi (mN/m)	$\pm$
0	65.905	0.007
25	59.418	0.010
50	55.291	0.010
75	51.972	0.009
100	51.093	0.010
125	49.773	0.009
150	49.161	0.009
175	47.231	0.009
200	46.884	0.010
225	46.417	0.010
250	43.454	0.008
300	42.887	0.009
350	41.298	0.009
400	40.471	0.009
450	39.493	0.010
500	38.547	0.009
750	40.185	0.009
1000	39.663	0.010

**Table S2:** Surface tension measurement for **4** in water at 75°C

Conc. <sup>cuvette</sup> ( $\mu\text{M}$ )	Pi (mN/m)	$\pm$
0	61.899	0,009
25	48.330	0,028
50	44.841	0,030
75	40.964	0,030
100	39.254	0,025
125	36.933	0,026
150	36.096	0,024
175	34.475	0,029
200	33.829	0,027
225	33.286	0,026
250	32.313	0,028
300	31.875	0,029
350	30.893	0,025
400	31.212	0,026
450	30.626	0,030
500	30.542	0,027
750	29.841	0,026

### General procedure for the recycling process

After performing a typical Suzuki-Miyaura cross coupling reaction (Figure 1, 1-6) as described in the previous section,  $\text{Cs}_2\text{CO}_3$  (1 mmol), boronic acid (1.2 mmol) and aryl halide (1 mmol) were added to the remaining aqueous phase (Figure 1, 7). The reaction media was then stirred for 30 min at 100 °C (Figure 1, 2-3). After cooling to room temperature, the coupling product was extracted with 3 x 5 mL of  $\text{Et}_2\text{O}$  (Figure 1, 4-5). The organic phase was then dried over  $\text{MgSO}_4$ , the solvent was evaporated *in vacuo* and the desired product was purified by flash column chromatography on silica gel to obtain the pure product (Figure 1, 6). The aqueous phase is once again available for subsequent cycles (Figure 1, 7).



**Figure S2:** biphasic mixture of ether and water (figure 1, 5) a) 4:1 Pd catalytic solution b) 5:1 Pd catalytic solution. Major palladium leaching is observed in the presence of 5.

**Table S3:** Isolated yields for each cycle of the recycling process

No. Cycles	Isolated Yields
1	95
2	95
3	95
4	95
5	94
6	93
7	92
8	90
9	86
10	80

## Dynamic light scattering (DLS) measurements of **4** in water

**Table S4<sup>a</sup>**: Diameter obtained from DLS measurements in water. Mono- or bis-imidazol-2-ylidene: Pd (**4**:Pd) species aggregate in larger micelles, due to the change of size and shape of the monomeric unit.

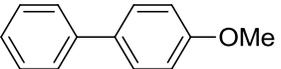
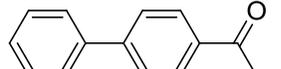
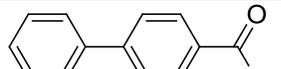
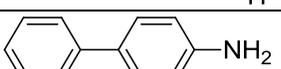
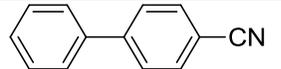
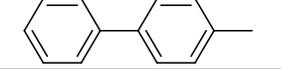
Sample	Conc. <b>4</b> (mM)	T (°C)	Size (nm)
<b>4</b>	1	25	17.43 ± 0.5
<b>4</b>	1	75	18.45 ± 0.5
<b>4</b>	1	90	14.05 ± 0.5
<b>4</b> :Pd <sup>b</sup>	1	90	139.30 ± 1.8
<b>4</b> :Pd (recycled) <sup>b</sup>	1	90	134.20 ± 1.7

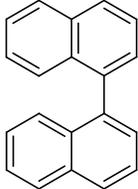
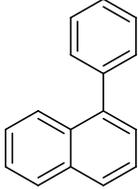
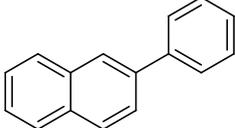
<sup>a</sup> The reactions were performed as described in the general procedure for the recycling process.

<sup>b</sup> Solutions prepared as described in Table 5 of the article.

<sup>c</sup> DLS measurement of the catalytic solution.

## Substrate scope references

Entry	Product	RMN
1		3
2		3
3		4
4		5
5		3
6		6
7		3

8		7
9		7
10		7

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